NASA-CR-194270

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SEMIANNUAL PROGRESS REPORT #4

For the Period
May 16, 1993 to November 15, 1993

KINETICS OF PHASE TRANSFORMATIONS IN GLASS FORMING SYSTEMS
NASA Contract NAG8-898

Prepared for
George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Huntsville, AL 35812

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November 20, 1993

(NASA-CR-194270) KINETICS OF PHASE TRANSFORMATIONS IN GLASS FORMING SYSTEMS Semiannual Progress Report No. 4, 16 May - 15 Nov. 1993 (Missouri Univ.) 16 p
N94-20347
Unclas
G3/27 0194052

A. WORK COMPLETED

1. Nonisothermal Nucleation for $Li_2O.2SiO_2$ (LS_2) Glass:

In crystallization measurements using DTA the glass sample is scanned at different constant heating rates until it is crystallized. This means that the temperature range where nucleation can occur for the glass is scanned also at different rates which allows the glass to be nucleated for different time prior to crystallization. Consequently, the concentration of nuclei developed in the glass may be different for different heating rates and the DTA peak height which has been shown to be sensitive to the number of nuclei present in the sample, is expected to change with heating rate.

The effect of nucleation heating rate, ϕ_n, (defined as the heating rate used to scan the temperature range where appreciable nucleation is believed to occur, 400 to 500°C for the LS_2 glass) on the DTA peak height, $(\delta T)_p$, was investigated using a LS_2 glass. Keeping the particle size (425 to 500 μm) and amount of sample (~ 35.9 mg) unchanged for different measurements, the glass was first heated in the DTA apparatus at a high heating rate (~ 100°C/min) from room temperature to about 400°C. After stabilizing at 400°C for ~2 min, the sample was first heated to 500°C using constant different heating rates (Nucleation Heating Rate, ϕ_n) and then heated at a constant heating rate (Crystallization Heating Rate, ϕ_c) until crystallization completed. The DTA peak heights obtained for the LS_2 glass at ϕ_n = 0.5, 1, 2, 4, 6, and 15°C/min and at a ϕ_c of 15°C/min were reported in our last progress report (#3, 11/16/92 to 5/15/93). These measurements were continued using different ϕ_c, namely, 2, 4, 6, 10, and 15°C/min and the results are shown in Fig 1. Fig 1 clearly shows that for a particular ϕ_c, $(\delta T)_p$ decreases initially with increasing ϕ_n indicating the formation of a less number of nuclei as the nucleation temperature region for this glass is scanned at a higher heating rate. This is what is expected since with increasing heating rate, the time required to scan the temperature region for nucleation decreases and the glass gets a shorter average time for nucleation. No appreciable change in $(\delta T)_p$ for this glass is observed when ϕ_n exceeds about 3°C/min, which suggests that no new nuclei is formed i.e., an embryo in the LS_2 glass does not get sufficient time to grow to a critical size when the heating rate is larger than 3°C/min. For many practical reasons, this limiting value of ϕ_n is considered to be an important parameter of a glass since it ensures a heating rate above which no new nuclei form in the glass.

Another important observation that results from this investigation is that the dependence of $(\delta T)_p$ on ϕ_c is stronger than its dependence on ϕ_n. This effect is clearly demonstrated in Fig 1 and is also separately shown in Fig 2. At low ϕ_c (crystallization heating rate), $(\delta T)_p$ does not change significantly with ϕ_n (nucleation heating rate). Calculations show that $(\delta T)_p$ at any ϕ_n increases by the same factor as that by which the ϕ_c is increased. The temperature at the maximum of the DTA crystallization peak, T_p, also increases with increasing ϕ_c as expected, but is nearly independent of ϕ_n, see Figs 3 and 4. The area of the DTA peak, which is a measure of the heat of crystallization, is also independent of ϕ_n for this LS_2 glass, but increases almost linearly with increasing ϕ_c, see Figs 5 and 6. The activation energy for crystallization, E_c, for these LS_2 glasses having different nucleation heat treatment was also determined using Kissinger method. It was observed that E_c was nearly independent of the nucleation heating rate and was ~ 300 ± 10 kJ/mol.

2. *Dependence of DTA Peak Height on the Total Number of Nuclei:*

In our previous progress reports (#2 and 3), it was demonstrated using a simple mathematical model that the DTA peak height, $(\delta T)_p$, depends strongly on the overlap between the nucleation rate (I) and growth rate (U) curves. In these calculations, it was assumed that $(\delta T)_p$ was directly proportinal to the total number of nuclei present in the glass sample under investigation, which, in turn, should be proportional to the volume or weight of the sample. To verify this assumption, DTA measurements were made using a LS_2 glass to determine $(\delta T)_p$ as function of sample weight. The measurements were made in nitrogen at a heating rate of 15°C/min using glass particles of 425 to 500 μm. The linear increase of measured $(\delta T)_p$ with increasing sample weight in Fig 7 demonstrates that $(\delta T)_p$ is linearly proportional to the total number of nuclei present in the glass and justifies the assumption made in our previous calculations.

3. Nucleation and Crystallization of $BaO.2SiO_2$ (BS_2) Glass:

A nucleation rate like curve was determined for the $BaO.2SiO_2$ (BS_2) glass using the DTA peak height technique, which showed that the temperature for nucleation ranged from 650 to 750°C for this glass and the temperature for maximum nucleation was ~ 705°C. These values are in excellent agreement with those determined by conventional technique. The activation energy for this glass, as determined by Kissinger method, was 495 ± 10 kJ/mol, which is much higher than the 300 kJ/mol for the LS_2 glass. Preliminary investigations suggest that the I and U curves overlap considerably for this glass. Further measurements to determine the extent of overlap between the nucleation and growth rate curves for this glass are continuing.

B. INTERNATIONAL COLLABORATION

(1) WITH JAPAN

Our international collaboration with the Osaka National Research Institute (ONRI), Japan continued during this reporting period. As mentioned in the progress report #2 (5/16/92 to 11/15/92), UMR conducted four experiments on the evaporation and rapid solidification of a $Na_2O.4TeO_2$ melt in low gravity using the 10 second drop shaft at the Japan Microgravity Center (JAMIC). These drop experiments were made available to UMR by JAMIC at no charge (cost of one drop is ~ $8000) and the travel expenses such as air fare and living expenses in Japan for the UMR scientists were provided by the Government of Japan. The samples recovered from the four drop experiments were brought back to UMR for analysis. The expenses for ground experiments at UMR and analysis of the drop shaft samples were provided by the UMR/MSM (Missouri School of Mines) Alumni Association.

The analyses of the drop shaft samples were completed recently at UMR, but some aspects of this work still continue. Several interesting and surprising results, which are consistent and reproducible in all four experiments, were obtained. The species evaporating from this sodium tellurite melt (~ 40 mg) formed a spherically symmetrical cloud which grew to a diameter of ~ 2.8 cm in 10 seconds of low gravity. Of course, no such nearly stagnant, spherical cloud was formed in similar experiments conducted at 1-g due to gravity-driven convection. The smoke cloud produced in low gravity was composed of spherical particles of pure TeO_2 whose average diameter was between 3 and 5 μm. These particles were 4 to 5 times larger than particles grown from similar experiments conducted at 1-g.

The most surprising and unexpected result from the drop shaft experiments was the total crystallizaion of rapidly quenched droplets of this glass forming melt.

Portions of the melt were detached from the platinum heating coil holding the melt during the high gravity period of capsule braking. These droplets were splattered onto a glass plate which formed the bottom of a rectangular glass box that enclosed the heating coil and the melt. Several completely crystallized splatters, 2 to 5 mm in diameter, 200 to 1200 μm thick and weighing only 5 to 15 mg, were recovered from all four experiments. This $Na_2.4TeO_2$ melt is a good glass former and glass bars several cm in size can be easily produced at 1-g without crystallization. The cooling rate for the drop shaft splatters is estimated as high as 200 to 400°C/s, so the rapid crystallization of these small pieces is totally unexpected. Why these very small pieces of rapidly quenched tellurite melt crystallized in the drop shaft experiments is unexplained at this time. A final report describing the results of the drop shaft experiments have been prepared for the different Japanese organizations, who supported this research. A copy of this report is attached.

As a part of this continued collaboration, experiments similar to those conducted in the drop shaft have been conducted recently aboard a Japanese aircraft where $\sim 10^{-4}$ g was obtained for about 20 seconds. The same $Na_2O.4TeO_2$ melt was used in order to compare the aircraft results with the results from the drop shaft experiments. The samples are now being analyzed at UMR.

(2) WITH GERMANY

One possible explanation for the rapid crystallization of the tellurite melt in the drop shaft experiments (reported above) is the shock wave that could be produced (by impact) in the melt during the high gravity period of capsule braking (deceleration). To examine this hypothesis, a collaboration has been established with Professor G. H. Frischat of the Technical University at Clausthal, Germany. According to our present plans, this tellurite glass will be remelted and solidified at different gravity levels produced in a high temperature centrifuge at Clausthal. With this centrifuge, gravity levels upto 255 times the normal gravity can be produced. The furnace can achieve a maximum temperature of 1400°C and is capable of heating or cooling at 30°C/min. The $Na_2O.4TeO_2$ glass to be used for the high temperature centrifuge experiments has been prepared and sent to Professor Frischat. After melting/quenching in the centrifuge, the samples will be returned to UMR for analysis.

C. WORK IN PROGRESS/PLANNED

(1) Determine the effect of platinum (heterogeneous) nucleation on the nucleation rate curve for the LS_2 glass. Lithium disilicate glasses containing different concentration of platinum have been prepared. The nucleation rate curve for these glasses will be determined using the DTA peak height and peak temperature techniques. The extent of overlap between the nucleation and growth rate curves will be assessed as a function of platinum concentration. The nucleation rate curve for these glasses will also be determined by conventional technique using transmission electron microscopy (TEM) at the Washington University at St. Louis. The glass samples for TEM measurements have also been prepared and provided to Dr. K. F. Kelton of Washington University.

(2) Measure dielectric constant and dissipation factor for the LS_2 glass as a function of nucleation and crystallization temperature. Since the dielectric constant (ϵ) and the dissipation factor (tan δ) depend upon the volume percent of the crystals present in the glass, it is believed that these two properties can also be used to estimate the nucleation and growth rates for a glass. Samples of a lithium disilicate glass of about 3 mm thick have been prepared for these measurements. These samples will be given different nucleation and crystal growth heat treatment,

polished, and gold coated on both sides prior to measuring ϵ and $\tan\delta$. Attempts will be made to correlate ϵ or $\tan\delta$ with the nucleation or crystal growth temperatures.

(3) Continue measurements on the nucleation rate curve for the BS_2 glass. The measurements are being conducted on the undoped glass at this time. After completing this work, the effect of platinum nucleation on the DTA peak height and peak temperature for this glass will also be investigated.

(4) Continue international collaboration with the Osaka National Research Institute (ONRI), Japan and Technical University at Clausthal, Germany, to investigate the evaporation and solidification of a sodium tellurite melt at low and high gravity.

D. PRESENTATION/PUBLICATION

1. C. S. Ray, D. S. McIntyre, and D. E. Day, "Studies on Nucleation and Crystallization of Glasses by DTA", presented at the 94th Annual Meeting of the American Ceramic Society, Minneapolis, MN, 12-16 April, 1992.

2. C. S. Ray and D. E. Day, "Nucleation and Crystallization in Glasses by DTA", Ceramic Transactions: Nucleation and Crystallization in Liquids and Glasses, Ed. M. C. Weinberg, Vol. 30, pp 207-223 (1993), American Ceramic Society Inc., Westerville, OH.

3. T. S. Cull, K. F. Kelton, and C. S. Ray, "Numerical Simulation of Nonisothermal Crystallization of Lithium Disilicate Glass", presented at the Midwest Solid Conference, University of Missouri-Columbia, Columbia, MO, September, 1993

4. K. F. Kelton, T. S. Cull, C. S. Ray, and D. E. Day, "Computer Simulation of Nonisothermal Phase Transformations", to be presented at the 8th Annual

Symposium on Microgravity Science and Space Processing, Reno, Nevada, 10-13 January, 1994.

5. J. K. R. Weber, D. R. Merkeley, C. D. Anderson, P. C. Nordine, C. S. Ray, and D. E. Day, "Enhanced Formation of Calcia-Gallia Glass by Containerless Processing", J. Am. Ceram. Soc., **76**, 2139-41 (1993).

6. W. Huang, C. S. Ray, and D. E. Day, "The Determination of Nucleation Rate Curve in the Crystallization Process of Glasses from DTA Technique", Journal of Shanghai Institute of Building Materials (in Chinese), **6** [3], 187-195 (1993).

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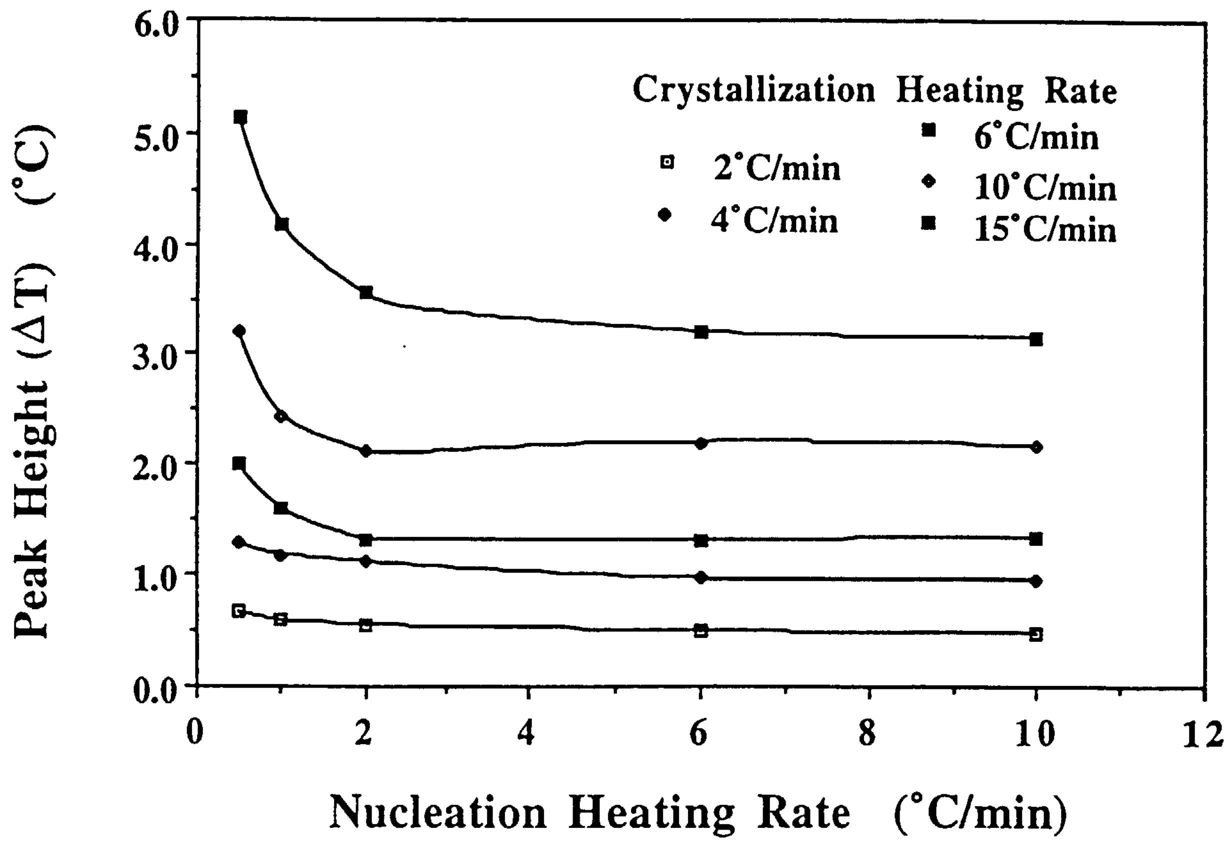

Fig 1. DTA peak height for a $Li_2O.2SiO_2$ glass as a function of nucleation heating rate, ϕ_n, and at constant crystallization heating rate, ϕ_c. Sample weight: 35.9 mg. Particle size: 425 to 500 μm.

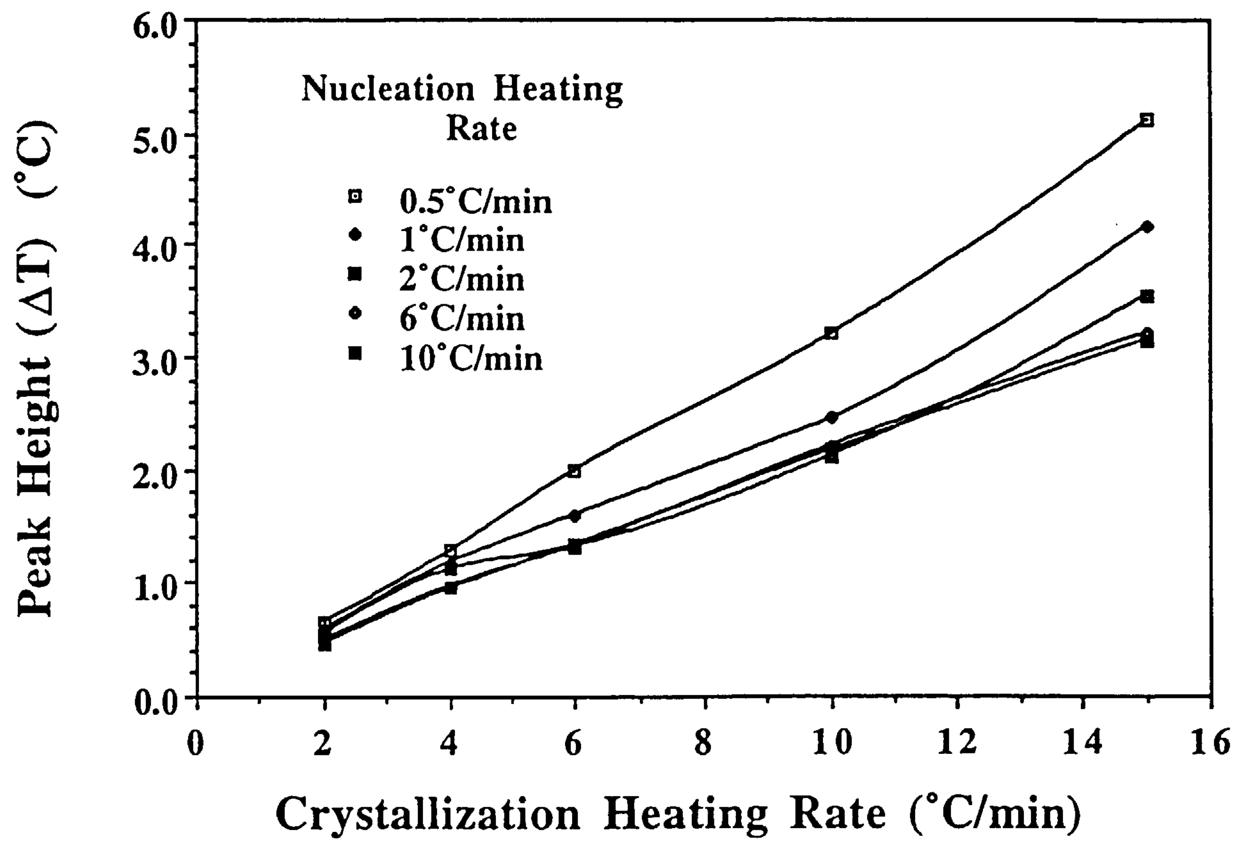

Fig 2. DTA peak height for a $Li_2O.2SiO_2$ glass as a function of crystallization heating rate, ϕ_c, and at constant nucleation heating rate, ϕ_n. Sample weight: 35.9 mg. Particle size: 425 to 500 μm. Figs 1 and 2 are same but plotted differently. Both figures show that DTA peak heights for this glass depends more strongly on ϕ_c than on ϕ_n.

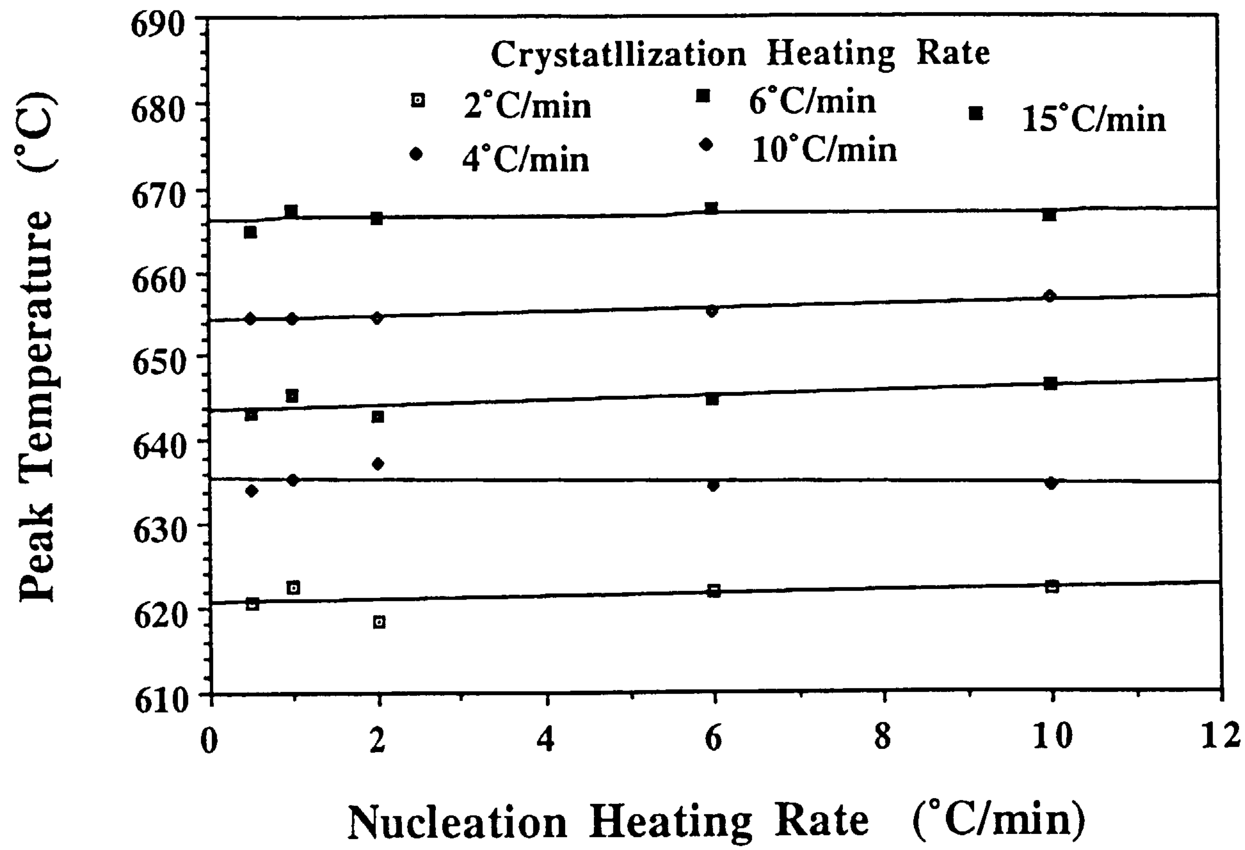

Fig 3. DTA peak temperature for a $Li_2O.2SiO_2$ glass as a function of nucleation heating rate, ϕ_n, and at constant crystallization heating rate, ϕ_c. Sample weight: 35.9 mg. Particle size: 425 to 500 μm.

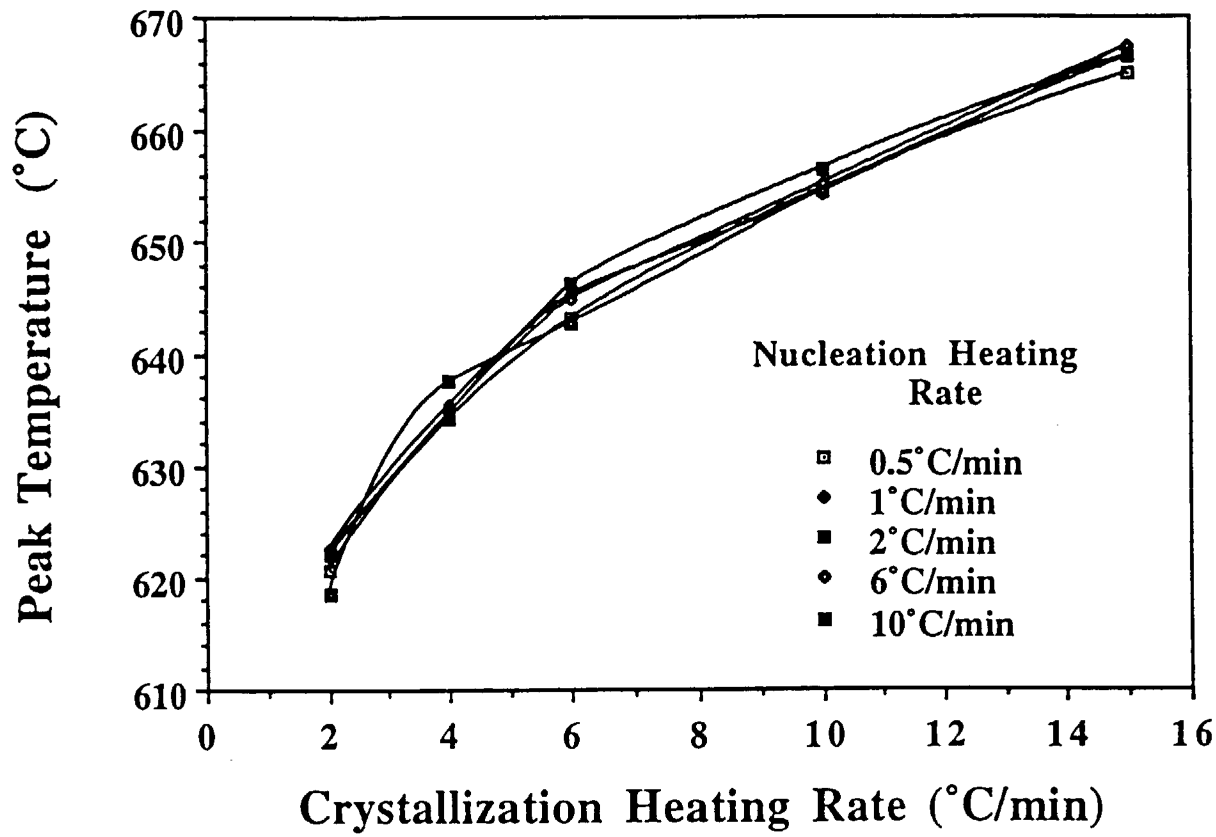

Fig 4. DTA peak temperature for a $Li_2O.2SiO_2$ glass as a function of crystallization heating rate, ϕ_c, and at constant nucleation heating rate, ϕ_n. Sample weight: 35.9 mg. Particle size: 425 to 500 μm. Figs 3 and 4 are same but plotted differently. Both figures show that DTA peak temperature for this glass depends strongly on ϕ_c, but is nearly independent of ϕ_n.

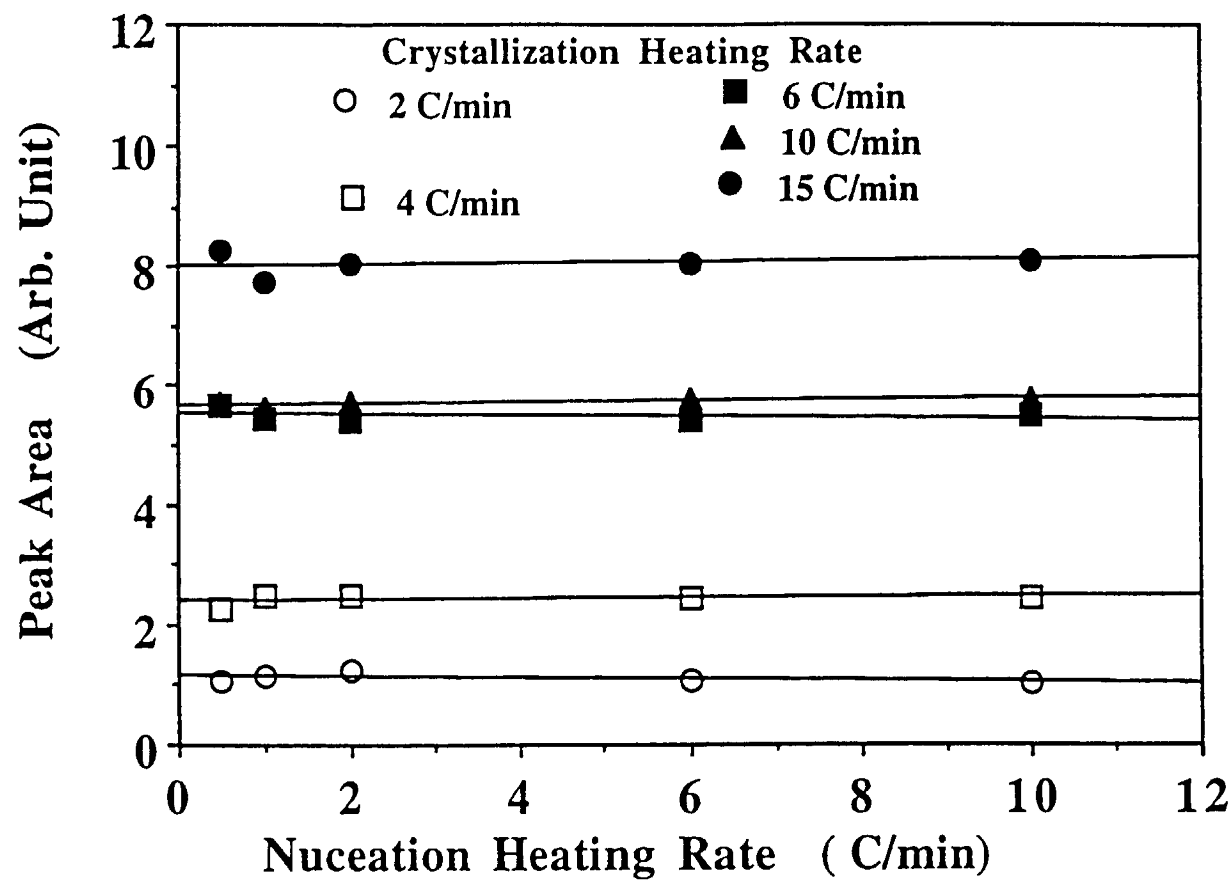

Fig 5. DTA crystallization peak area (in arbitrary unit, but all measured in same scale) for a $Li_2O.2SiO_2$ glass as a function of nucleation heating rate, ϕ_n, and at constant crystallization heating rate, ϕ_c. Sample weight; 35.9 mg. Particle size: 425 to 500 μm.

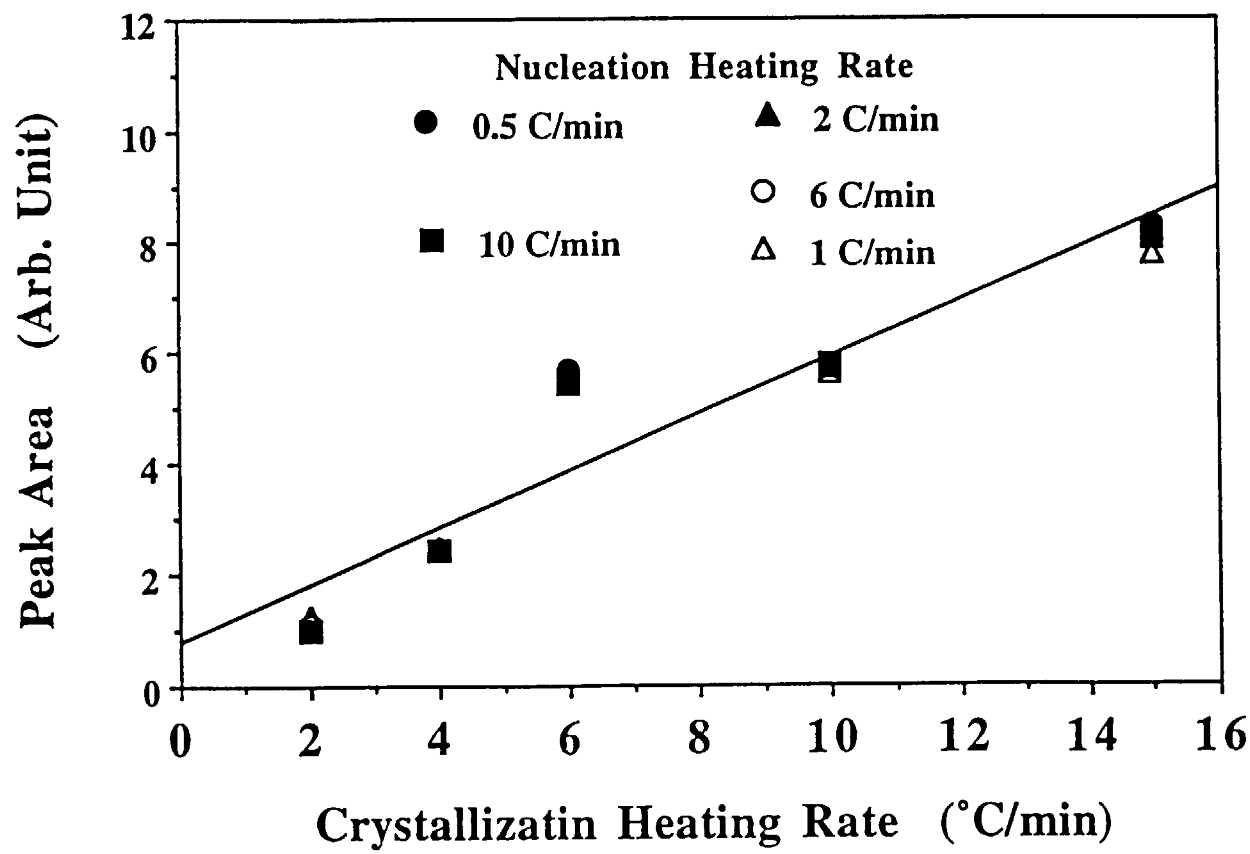

Fig 6. DTA crystallization peak area (in arbitrary unit, but all measured in same scale) for a $Li_2O.2SiO_2$ glass as a function of crystallization heating rate, ϕ_c, and at constant nucleation heating rate, ϕ_n. Sample weight: 35.9 mg. Particle size: 425 to 500 μm. Figs 5 and 6 are same but plotted differently. Both figures show that like DTA peak temperature, peak area which is measure of the heat of crystallization, depends strongly on ϕ_c, but is nearly independent of ϕ_n.

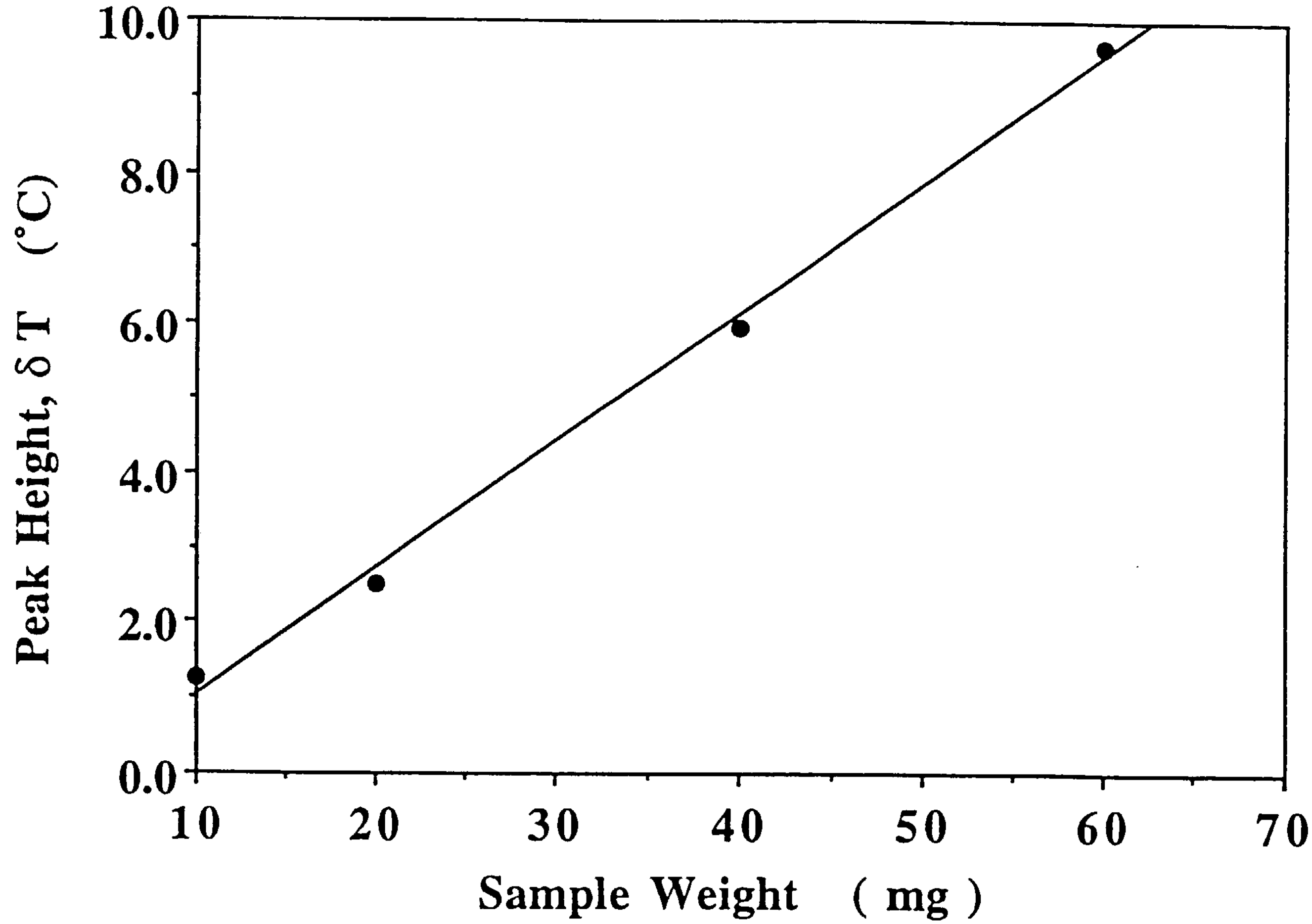

Fig 7. DTA peak height for a $Li_2O.2SiO_2$ glass as a function of sample weight. Particle size: 425 to 500 μm. DTA heating rate 15°C/min. The linear increase with increasing sample weight indicates that the DTA peak height is linearly proportional to the number of nuclei present in the glass.